

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C01B 3/36	A1	(11) International Publication Number: WO 97/22547 (43) International Publication Date: 26 June 1997 (26.06.97)
(21) International Application Number: PCT/EP96/05733 (22) International Filing Date: 11 December 1996 (11.12.96) (30) Priority Data: 95203535.0 18 December 1995 (18.12.95) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant (for all designated States except CA): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (71) Applicant (for CA only): SHELL CANADA LIMITED [CA/CA]; 400 - 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). (72) Inventors: OORTWIJN, Peter; Badhuisweg 3, NL-1031 CM Amsterdam (NL). WENTINCK, Hendrik, Martinus; Badhuisweg 3, NL-1031 CM Amsterdam (NL). MARTENS, Franciscus, Johanna, Arnoldus; Badhuisweg 3, NL-1031 CM Amsterdam (NL).		(81) Designated States: AU, BR, CA, CN, JP, KR, NO, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: A PROCESS FOR PREPARING SYNTHESIS GAS (57) Abstract A process for preparing synthesis gas by partial oxidation of a hydrocarbon-containing fuel in the absence of moderator gas, comprising the steps of: supplying a hydrocarbon-containing fuel and an oxidiser through a reactor mix type burner (i.e. wherein the said fuel and said oxidiser each flowing in one or more separate burner passages debouching into the gasification zone, are not mixed until immediately downstream of the burner passages) to a gasification zone under oxygen blast conditions (i.e. the velocity of the oxidiser is substantially larger than the velocity of the fuel at the outlet of the burner); and wherein at least the rim(s) of the burner internal(s) separating at least at or near its (their) tip(s) said fuel from said oxidiser is (are) made of ceramic material or a noble metal or a noble metal alloy or wherein the rim(s) of the burner internal(s) separating at least at or near its (their) tip(s) said fuel from said oxidiser is (are) provided at its (their) oxidiser side(s) with a lining of ceramic material or noble metal or a noble metal alloy.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

A PROCESS FOR PREPARING SYNTHESIS GAS

The present invention relates to a process for preparing synthesis gas by partial oxidation of a hydrocarbon-containing fuel and an oxygen-containing gas in the absence of moderator gas. In particular, liquid or gaseous hydrocarbon-containing fuel is applied.

In such a process for preparing synthesis gas an oxygen-containing gas, which is applied as an oxidiser, and a hydrocarbon-containing fuel are supplied to a gasification zone through a burner comprising an arrangement of passages or channels for fuel and oxidiser, and wherein autothermically a gaseous stream containing synthesis gas is produced under appropriate conditions. The passages or channels are separated from each other by separation walls, the so-called burner internals.

In many known processes for preparing synthesis gas a moderator gas (for example steam, water or carbon dioxide or a combination thereof) is supplied to the gasification zone in order to control the temperature in the gasification zone. Moderator gas may be added to the oxidiser or (gaseous) fuel or may be supplied via a moderator gas passage. Those skilled in the art will know the conditions of applying oxidiser and moderator gas.

Advantageously, a multi-orifice (co-annular) burner comprising a concentric arrangement of n passages or channels co-axial with the longitudinal axis of said burner, wherein n is an integer > 2 , is applied.

Such multi-orifice (co-annular) burners contain substantially cylindrical internals which separate the fluid streams flowing through the passages until they reach the burner exit. In particular, such multi-orifice

- 2 -

(co-annular) burners comprise an arrangement of annular concentric channels or passages for supplying oxidiser, moderator gas (optionally) and fuel to the gasification zone.

5 Multi-orifice (co-annular) burners are known as such and the mechanical structures thereof will therefore not be described in detail.

10 Usually such burners comprise a number of slits at the burner outlet and hollow wall members with internal cooling fluid (e.g. water) passages. The passages may or may not be converging at the burner outlet. Instead of comprising internal cooling fluid passages, the burner may be provided with a suitable ceramic or refractory lining applied onto or suspended by a means closely
15 adjacent to the outer surface of the burner (front) wall for resisting the heat load during operation or heat-up/shut down situations of the burner. Advantageously, the exit(s) of one or more passages may be retracted or protruded with respect to the outer passage.

20 It will be appreciated by those skilled in the art that any slit width suitable for the purpose can be applied, dependent on the burner capacity.

Advantageously, the central passage has a diameter up to 70 mm, whereas the remaining concentric passages have
25 slit widths in the range of 1-30 mm.

However, it will be appreciated that the present application is not confined to the use of co-annular burners.

30 The oxidiser and the fuel and, optionally, moderator gas are supplied to the gasification zone through the respective channels at specific velocities and mass distribution in order to obtain a good atomization and mixing.

Advantageously the respective velocities are measured
35 or calculated at the outlet of the said respective

- 3 -

channels into the gasification zone. The velocity measurement or calculation can be carried out by those skilled in the art in any way suitable for the purpose and will therefore not be described in detail.

5 The oxygen-containing gas, which is applied as oxidiser, is usually air or oxygen or a mixture thereof. An oxidiser comprising at least 95% oxygen is preferred.

10 Synthesis gas is a gas comprising carbon monoxide and hydrogen, and it is used, for example, as a clean medium-calorific value fuel gas or as a feedstock for the synthesis of methanol, ammonia or hydrocarbons, which latter synthesis yields gaseous hydrocarbons and liquid hydrocarbons such as gasoline, middle distillates, lub oils and waxes.

15 In the specification and in the claims the term gaseous (liquid) hydrocarbon-containing fuel will be used to refer to hydrocarbon-containing fuel that is gaseous (liquid) at gasifier feed pressure and temperature.

20 According to an established process, synthesis gas is produced by partially oxidising in a reactor vessel a gaseous fuel such as a gaseous hydrocarbon, in particular petroleum gas or natural gas, at a temperature in the range of from 1000 °C to 1800 °C and at a pressure in the range of from 0.1 MPa to 12 MPa abs. with the use of an
25 oxidiser.

30 Synthesis gas will often be produced near or at a crude oil refinery because the produced synthesis gas can directly be applied as a feedstock for the production of middle distillates, ammonia, hydrogen, methanol or as a fuel gas, for example, for heating the furnaces of the refinery or more efficiently for the firing of gas turbines to produce electricity and heat.

35 For economic reasons it is often desirable to operate the burner without the application of a moderator gas. Further, in order to obtain a good mixing of fuel and

- 4 -

oxidiser in the gasifier it is preferred to operate the burner under such conditions that an oxygen blast exists (i.e. the velocity of the oxidiser is substantially larger than the velocity of the fuel at the outlet of the burner). Those skilled in the art will know these conditions.

It will be appreciated by those skilled in the art that oxygen blast permits lower fuel supply pressures and enables reduction of compression cost.

Usually, the rim of a burner internal (i.e. that part of the burner internal which, when the burner is mounted in a reactor vessel, is directed to the gasification zone and terminates in a tip) is made of steel or low alloy steel.

However, when applying oxygen blast in the absence of moderator gas it has appeared that the rim(s) of the burner internal(s) separating fuel and oxidiser is (are) severely attacked by metal dusting phenomena so that serious burner damage will occur and the burner lifetime is restricted.

Metal dusting is a catastrophic carburization which occurs in industrial plants under conditions of high activity and low oxygen pressure in the temperature range 600-800 °C, leading to decomposition of steels into a mixture of powdery carbon, metal particles and sometimes carbides and oxide. Pitting or general metal wastage is observed, if the corrosion product was carried away by erosion through the gas flow.

It is an object of the invention to provide an economically feasible process for preparing synthesis gas which can be carried out over a long period without the need for many shut downs.

The invention therefore provides a process for preparing synthesis gas by partial oxidation of a

- 5 -

hydrocarbon-containing fuel in the absence of moderator gas, comprising the steps of:

supplying a hydrocarbon-containing fuel and an oxidiser through a reactor mix type burner (i.e. wherein the said fuel and said oxidiser each flowing in one or more separate burner passages debouching into the gasification zone, are not mixed until immediately downstream of the said burner passages) to a gasification zone under oxygen blast conditions (i.e. the velocity of the oxidiser is substantially larger than the velocity of the fuel at the outlet of the burner); and wherein at least the rim(s) of the burner internal(s) separating at least at or near its (their) tip(s) said fuel and said oxidiser is (are) made of ceramic material or a noble metal or a noble metal alloy or wherein the rim(s) of the burner internal(s) separating at least at or near its (their) tip(s) said fuel and said oxidiser is (are) provided at its (their) oxidiser side(s) with a lining of ceramic material or noble metal or a noble metal alloy.

The invention further provides a reactor mix type burner to be used in such a process for preparing synthesis gas, said burner comprising an arrangement of at least a fuel burner passage and at least an oxidiser burner passage wherein at least the rim(s) of the burner internal(s) separating at least at or near its (their) tip(s) said fuel passage and said oxidiser passage is (are) made of ceramic material or noble metal or a noble metal alloy or wherein the rim(s) of the burner internal(s) separating at least at or near its (their) tip(s) said fuel passage and said oxidiser passage is (are) provided at its (their) oxidiser side(s) with a lining of ceramic material or noble metal or a noble metal alloy.

Advantageously, the said rim(s) of the said burner internal(s) separating said fuel and said oxidiser is

- 6 -

(are) made of a Pt alloy e.g. Pt/Rh, or Pt/Ir or any ceramic material suitable for the purpose, e.g. SiC (silicon carbide) or Si₃N₄ (silicon nitride).

5 The fuel is e.g. natural gas, which advantageously comprises at least 80% CH₄. Advantageously, the velocity ratio between oxidiser and fuel is:

$$\frac{V_{\text{fuel}}}{V_{\text{oxidiser}}} = 0.25-0.6.$$

More advantageously, the oxidiser velocity is 50-100 m/s and the fuel velocity is 25-60 m/s (provided that the above ratio is satisfied).

10 When applying the process of the invention it has been found that there is no metal dusting and that the burner lifetime is at least 1600 hours.

Advantageously the said rim(s) of the said burner internal(s) separating said fuel and said oxidiser has
15 (have) a length of 2-20 mm and a thickness of 0.3-1.0 mm and is (are) mechanically connected in any suitable manner to the burner internal e.g. by welding.

In another advantageous embodiment of the invention the rim(s) of the burner internal(s) separating the fuel
20 and the oxidiser is (are) provided with a lining (e.g. a ribbon) at the oxidiser side(s) of the burner internal(s). Such a ribbon may have a length of 5-10 mm and a thickness of 0.2-0.5 mm.

The invention will now be described by way of example
25 in more detail by reference to the drawing, in which the figure schematically represents a burner to be used in the process of the invention.

Referring to the figure, a partial longitudinal section of a burner having a central passage and an outer
30 passage has been shown schematically. X represents the axis of the burner. The burner debouches into a gasification zone G of a reactor through a refractory

- 7 -

dome. For reasons of clarity the burner has been shown partially only and the reactor details have not been shown. In particular, details of (water)-cooling of the burner have been omitted for reasons of clarity.

5 In the figure a substantially conical burner has been represented but it will be appreciated by those skilled in the art that any shape suitable for the purpose (e.g. substantially cylindrical) is possible.

10 A burner internal rim 1 and its tip 1a have been represented. The rim 1 is made of ceramic material (e.g. SiC or Si₃N₄) or noble metal (e.g. Pt) or a noble metal alloy (e.g. Pt/Rh or Pt/Ir) and is mounted on the burner internal 2 at its end directed to the gasification zone G, e.g. by welding.

15 Through the central passage 3 (diameter e.g. 41 mm) oxidiser is flowing whereas through the outer passage 4 fuel (e.g. natural gas) is flowing. Reference numeral 5 represents the outer passage wall. The slit width of the outer passage 4 is e.g. 25 mm.

20 The arrows A and B representing the velocities of the oxidiser (e.g. 100 m/s) and fuel (e.g. 50 m/s) respectively, indicate that an oxygen blast exists.

The invention will now be described by way of example in more detail by reference to Examples I and II.

25 Example I (oxygen blast).

Flow conditions at the rim between fuel passage and oxidiser passage are considered. The rim is made of Pt. Oxidiser is supplied through a central passage and fuel is supplied through a concentric outer passage.

- 8 -

Pressure		47	bara
Oxidiser			
Throughput O ₂ (>99 mol%)		400	tpd
oxidiser temp.		250	°C
oxidiser density		35	kg/m ³
Fuel			
Throughput	NG	350	tpd
NG composition	CH ₄	88.55	mol%
	C ₂ H ₆	3.85	mol%
	C ₃ H ₈	2.47	mol%
	C ₄ H ₁₀	1.15	mol%
	C ₅ H ₁₂	0.36	mol%
	C ₆ H ₁₈	0.24	mol%
	CO ₂	2.85	mol%
	N ₂	0.53	mol%
	fuel		
	temperature	400	°C
	fuel density	16	kg/m ³
burner outlet geometry: outer diameter oxidiser passage: 41 mm; outer diameter fuel passage: 90 mm			
Flow conditions at the rim between fuel passage and oxidiser passage			
	Fuel velocity	50	m/s
	Oxidiser velocity	100	m/s
	Fuel/Oxidiser velocity ratio	0.50	

Example II (fuel blast)

Flow conditions at the rim between fuel passage and oxidiser passage are considered. The rim is made of steel. Oxidiser is supplied through a central passage; fuel is supplied through a concentric outer passage.

- 9 -

Pressure		47	bara
Oxidiser			
Throughput	O ₂ (> 99 mol%)	400	tpd
	oxidiser temp.	250	°C
	oxidiser density	35	kg/m ³
Fuel			
Throughput	NG	350	tpd
NG composition	CH ₄	88.55	mol%
	C ₂ H ₆	3.85	mol%
	C ₃ H ₈	2.47	mol%
	C ₄ H ₁₀	1.15	mol%
	C ₅ H ₁₂	0.36	mol%
	C ₆ H ₁₈	0.24	mol%
	CO ₂	2.85	mol%
	N ₂	0.53	mol%
	fuel temperature	400	°C
	fuel density	16	kg/m ³
burner outlet geometry			
outer diameter oxidiser passage: 65 mm			
outer diameter fuel passage: 86 mm			
Flow conditions at the rim between fuel passage and oxidiser passage			
	Fuel velocity	100	m/s
	Oxidiser velocity	40	m/s
	Fuel/Oxidiser velocity ratio	2.5	

In Example I the burner was inspected after 2300 hours of operation without moderator gas. No visible damage was detected and the burner was in good condition.

- 10 -

In Example II it appeared that the rim between fuel passage and oxidiser passage was severely attacked after approximately 1000 hours of operation.

5 Various modifications of the present invention will become apparent to those skilled in the art from the foregoing description. Such modification are intended to fall within the scope of the appended claims.

- 11 -

C L A I M S

1. A process for preparing synthesis gas by partial oxidation of a hydrocarbon-containing fuel in the absence of moderator gas, comprising the steps of:

supplying a hydrocarbon-containing fuel and an oxidiser through a reactor mix type burner (i.e. wherein the said fuel and said oxidiser each flowing in one or more separate burner passages debouching into the gasification zone, are not mixed until immediately downstream of the said burner passages) to a gasification zone under oxygen blast conditions (i.e. the velocity of the oxidiser is substantially larger than the velocity of the fuel at the outlet of the burner); and wherein at least the rim(s) of the burner internal(s) separating at least at or near its (their) tip(s) said fuel and said oxidiser is (are) made of ceramic material or noble metal or a noble metal alloy or wherein the rim(s) of the burner internal(s) separating at least at or near its (their) tip(s) said fuel and said oxidiser is (are) provided at its (their) oxidiser side(s) with a lining of ceramic material or noble metal or a noble metal alloy.

2. The process as claimed in claim 1, wherein the velocity ratio V_{fuel}

$$\frac{\quad}{V_{\text{oxidiser}}} = 0.25-0.6.$$

3. The process as claimed in claims 1 or 2, wherein the velocity of the oxidiser is 50-100 m/s and the velocity of the fuel is 25-60 m/s (provided that an oxygen blast exists).

4. The process as claimed in any one of claims 1-3, wherein the fuel is gaseous or liquid.

- 12 -

5. The process as claimed in claim 4, wherein the fuel is natural gas.

6. The process as claimed in claim 5, wherein the natural gas comprises at least 80% CH₄.

5 7. The process as claimed in any one of claims 1-6, wherein the said rim(s) of the said burner internal(s) separating the said fuel and the said oxidiser is (are) made of a Pt alloy e.g. Pt/Rh or Pt/Ir or made of ceramic material e.g. silicon nitride or silicon carbide.

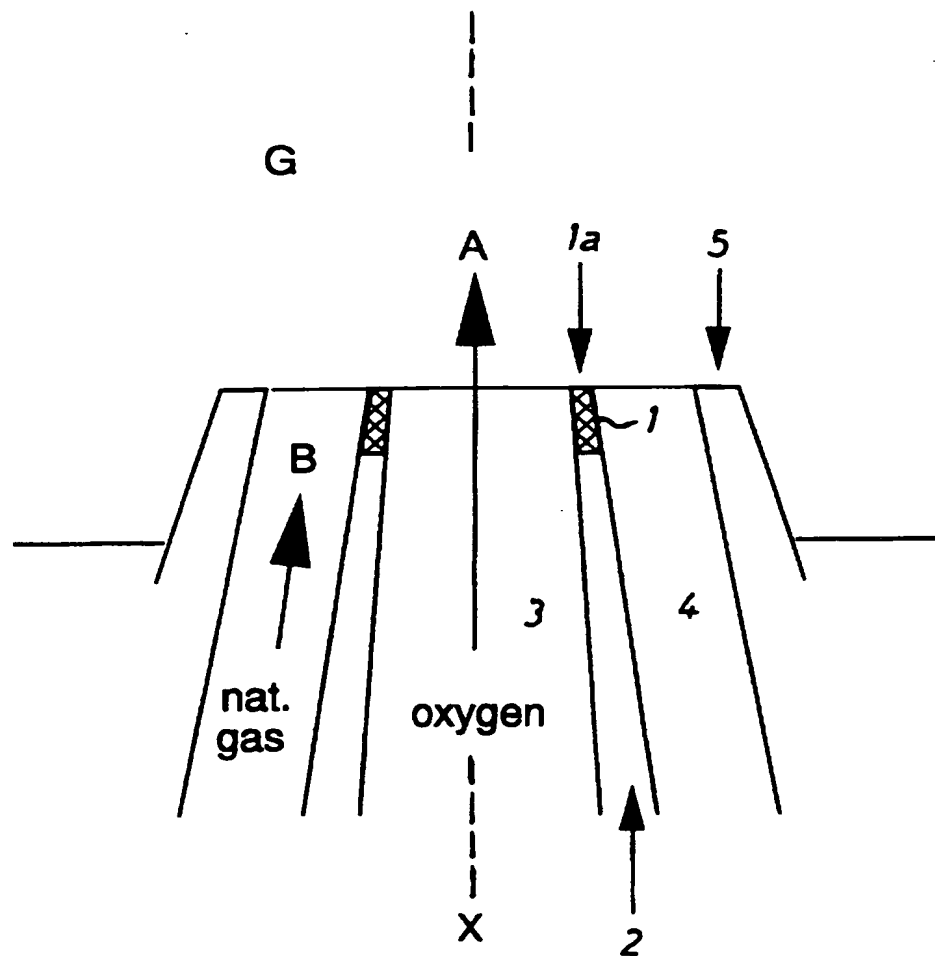
10 8. The process as claimed in any one of claims 1-7, wherein the said rim(s) of the said burner internal(s) separating the said fuel and the said oxidiser has (have) a length of 2-20 mm, and a thickness of 0.3-1.0 mm.

15 9. The process as claimed in any one of claims 1-8, wherein the burner is a co-annular burner comprising a concentric arrangement of n passages or channels co-axial with the longitudinal axis of said burner, wherein n is an integer > 2.

20 10. A reactor mix type burner to be used in the process as claimed in any one of claims 1-9, comprising an arrangement of at least a fuel burner passage and at least an oxidiser burner passage wherein at least the rim(s) of the burner internal(s) separating at least at or near its (their) tip(s) said fuel and said oxidiser is
25 (are) made of ceramic material or noble metal or a noble metal alloy or wherein the rim(s) of the burner internal(s) separating at least at or near its (their) tip(s) said fuel and said oxidiser is (are) provided at
30 its (their) oxidiser side(s) with a lining of ceramic material or noble metal or a noble metal alloy.

11. Synthesis gas whenever obtained by the process as claimed in any one of claims 1-9.

1/1



INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/EP 96/05733

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B3/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 098 043 A (TEXACO DEVELOPMENT CORP.) 11 January 1984 see page 18, line 28 - line 31; claim 1 ---	1
A	EP 0 184 164 A (BASF AG) 11 June 1986 see claim 3 ---	1
A	EP 0 312 133 A (SHELL INT RESEARCH) 19 April 1989 see claim 1 ---	1
A	EP 0 545 281 A (HOECHST AG) 9 June 1993 see claim 1 ---	1
A	EP 0 288 387 A (AZOTE & PROD CHIM) 26 October 1988 see column 2, line 56 - column 3, line 8; claim 1 --- -/-	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

11 March 1997

Date of mailing of the international search report

27.03.97

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Clement, J-P

INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/EP 96/05733

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 343 735 A (SHELL INT RESEARCH) 29 November 1989 see claim 1</p> <p>-----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. al Application No

PCT/EP 96/05733

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 98043 A	11-01-84	US 4443228 A AU 558256 B AU 1573883 A CA 1190046 A JP 59022991 A US 4491456 A	17-04-84 22-01-87 05-01-84 09-07-85 06-02-84 01-01-85
EP 0184164 A	11-06-86	DE 3444336 A JP 61136901 A	05-06-86 24-06-86
EP 0312133 A	19-04-89	AU 2199788 A CA 1308644 A DE 3864790 A JP 1107012 A US 4878835 A	16-03-89 13-10-92 17-10-91 24-04-89 07-11-89
EP 0545281 A	09-06-93	DE 4140063 A AU 649599 B AU 2992292 A CA 2084035 A CN 1073472 A JP 5239473 A JP 6070228 B US 5273212 A ZA 9209235 A	09-06-93 26-05-94 10-06-93 06-06-93 23-06-93 17-09-93 07-09-94 28-12-93 12-07-93
EP 0288387 A	26-10-88	FR 2614294 A	28-10-88
EP 343735 A	29-11-89	AT 136525 T AU 611803 B AU 3514089 A CA 1321878 A CN 1038069 A DE 68926180 D DE 68926180 T ES 2085859 T GB 2219003 A JP 2043288 A PT 90650 B US 4888031 A	15-04-96 20-06-91 30-11-89 07-09-93 20-12-89 15-05-96 29-08-96 16-06-96 29-11-89 13-02-90 31-10-94 19-12-89